

## A Coulometric Technique for Monitoring the Morphology of Copper Electrodeposits

L.D. Burke and A. M. O'Connell

Chemistry Department, University College Cork,  
Cork, Ireland.

The real surface area, or roughness, of a surface is a useful indication of the form or morphology of a metal electrodeposit and is often employed in the studies of the effects of bath additives and in monitoring the performance of the plating bath. Some of the more sophisticated techniques for determining real surface area, e.g. STM and AFM, are relatively expensive, not always suitable to a production environment and probably have difficulty accessing and accurately monitoring the internal surfaces of relatively rough surfaces. Coulometric techniques, based on the use of cyclic voltammetry, are much cheaper and more convenient to operate and are well established in the noble metal electrochemistry area (1). The use of this approach to monitor the roughness of copper electrodeposits, and to investigate how this roughness is influenced by the presence of bath additives such as thiourea, will be described.

It is now well established (2) that copper produced by electrodeposition is not the conventional metal but an active, metastable state of copper. It is generally accepted that active states are highly defective, i.e. they contain an unusually high density of extended vacancies, grain boundaries and minute grains. The activities of such states also tend to decay with time (this again has been observed (2) with electrodeposited copper). The influence of bath additives is usually explained in terms of the effect of adsorption of such species at the metal electrode surface. This may well be valid; however, a more important effect may be the adsorption of the additive on the freshly created, nascent, copper nuclei. Such adsorption is assumed to inhibit the growth of the nuclei, increase the overpotential for a given plating rate and yield an initially highly active copper layer. Evidence to support these assumptions will be presented.

### REFERENCES

1. R. Woods, *Electroanalytical Chemistry*, Vol. 9, Dekker, New York (1976), pp. 1 – 162.
2. P.C. Andricacos, *Electrochem. Soc. Interface*, 7 (1998) 23.

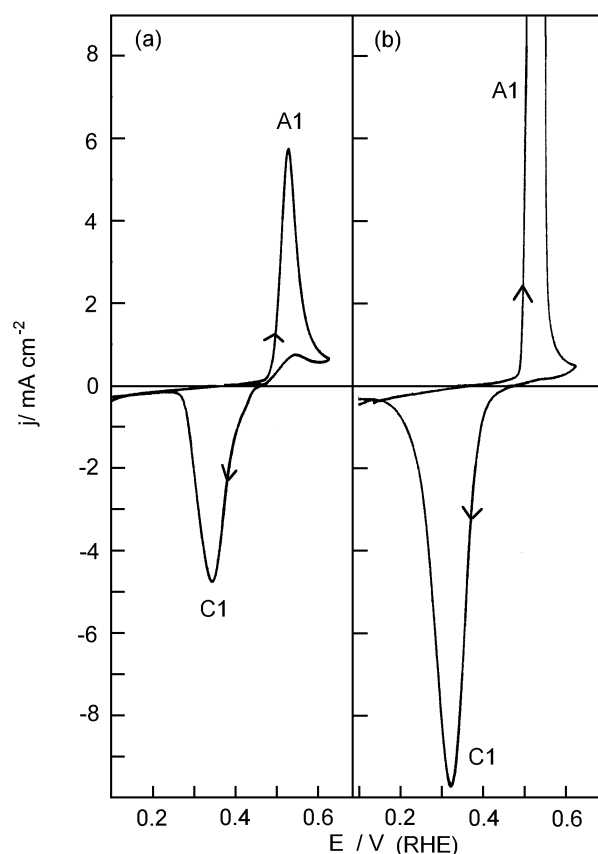


Fig. 1 Cyclic voltammogram (0.1-0.64 V, 5 mVs<sup>-1</sup>) for electrodeposited copper (on a gold wire electrode) in 1.0 mol dm<sup>-3</sup> NaOH at 60 °C. The copper was deposited at ambient temperature from a stirred solution of composition (a) 2.2 mol dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub>, 0.25 mol dm<sup>-3</sup> CuSO<sub>4</sub>·5H<sub>2</sub>O, 0 ppm thiourea, Q<sub>C1</sub>= 83 mC cm<sup>-2</sup> (b) 2.2 mol dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub>, 0.25 mol dm<sup>-3</sup> CuSO<sub>4</sub>·5H<sub>2</sub>O, 100 ppm thiourea, Q<sub>C1</sub>= 203 mC cm<sup>-2</sup>: the increased C1 charge in (b) reflects the greater surface area or roughness of the deposit formed in the presence of thiourea.